

# REPORT DOCUMENTATION PAGE

AFRL-SR-AR-TR-04-

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering the required data, completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188). Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not have a valid OMB control number. **PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.**

1. REPORT DATE (DD-MM-YYYY) 26-10-2004			2. REPORT TYPE STTR Phase I Final			3. DATES COVERED (from - to) 15 Sept 2003 - 15 Sept. 2004		
4. TITLE AND SUBTITLE Nanocomposites for Carbon Fiber Reinforced Polymer Matrix Composites						5a. CONTRACT NUMBER F49620-03-C-0093		
						5b. GRANT NUMBER		
						5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S) 1. Koo, J. H.      6. Weispfenning, J. 2. Pilato, L. A. 3. Wissler, G. 4. Lee, A. 5. Abusafieh, A.						5d. PROJECT NUMBER		
						5e. TASK NUMBER		
						5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) 1. University of Texas at Austin, Dept. of Mechanical Engineering, 1 University Station, C2200, Austin, TX 78712-0292 2. & 3. KAI, Inc. 6402 Needham Lane, Austin, TX 78739 4. Michigan State Univ. Dept. of Chemical Engr. And Material Science, East Lansing, MI 48823						8. PERFORMING ORGANIZATION REPORT NUMBER 5. & 6 Cytec Engineered Materials 1440 N. Kraemer Blvd., Anaheim, CA 92806		
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Dr. Charles Y-C Lee AFOSR/NL 4015 Wilson Blvd., Room 713 Arlington, VA 22203-1954						10. SPONSOR/MONITOR'S ACRONYM(S) AFOSR		
						11. SPONSOR/MONITOR'S REPORT NUMBER(S)		
12. DISTRIBUTION / AVAILABILITY STATEMENT  Approved for public release; distribution unlimited								
13. SUPPLEMENTARY NOTES  <div style="text-align: center; font-size: 2em; font-weight: bold;">20041109 014</div>								
14. ABSTRACT The major objective of this material program is to develop an improved epoxy nanocomposite for carbon fiber-reinforced polymer matrix composite (CPMC) with higher temperature performance capability, mechanical performance, damage resistance, extreme environment corrosion resistance, and improved dimensional control. We proposed that a nanophase be introduced into specific components of an epoxy resin system, prior to cure, to provide improved T <sub>g</sub> and mechanical strength of the composites. In this study, we used Cytec Engineered Materials (CEM) CYCOM® 977-3, a high temperature damage tolerant tetrafunctional epoxy resin system; and three types of nanoparticles: chemically modified montmorillonite (MMT) organoclays, surface treated nanosilica, and surface modified carbon nanofibers (CNF) to create new types of epoxy nanocomposites. The TEM analyses indicated that the MMT clay, nanosilica, and CNF dispersed very well in the epoxy resin system. Evidence is presented that a nanophase is formed when nanoparticles such as surface treated clay, surface treated nanosilica, or carbon nanofibers are introduced into the epoxy resin. Higher T <sub>g</sub> and complex modulus values from DMTA for the nanomodified materials are presented as evidence for nanophase presence in the epoxy resin system as compared to lower T <sub>g</sub> and complex modulus for the epoxy resin control. The DMTA data of the neat epoxy nanosilica nanocomposite (2% Aerosil® R202) show the highest T <sub>g</sub> (258°C) and the highest complex modulus (964 MPa). Five epoxy nanocomposites were selected to produce prepregs using AS4-6K carbon woven cloth at CEM. The prepregs were fabricated into composites. A set of two 18- by 11- by 0.15-inch composite panels was fabricated for physical, thermal, and mechanical properties characterization. Mechanical properties such as G <sub>1C</sub> , G <sub>2C</sub> , flatwise tension strength, short beam shear strength, and flexural strength were determined on the epoxy nanocomposites PMCs and compared with the baseline 977-3/AS4-K6 material. The resulting NCPMC were equal to or better than the baseline 977-3/AS4-K6 in short beam shear, flexural strength, and flatwise tension strength but deficient in G <sub>12</sub> and G <sub>2C</sub> values.								
15. SUBJECT TERMS STTR Report, Polymer Nanocomposites, Carbon Fiber Reinforced Polymer Matrix Composites, 977-3 Toughened Epoxy, Nanophase, Surface Modified MMT Clay, Nanosilica, Carbon Nanofiber, Epoxy, TEM, WAXD, Short Beam Shear Strength, Flatwise Tension Strength, and Flexural Strength, Mechanical Properties.								
16. SECURITY CLASSIFICATION OF:						17. LIMITATION OF ABSTRACT  U	18. NUMBER OF PAGES  33	19a. NAME OF RESPONSIBLE PERSON Joseph H. Koo, Sc.D.
a. REPORT U	b. ABSTRACT U	c. THIS PAGE U	19b. TELEPHONE NUMBER (include area code) (512) 589-4170					

# TABLE OF CONTENTS

Section	Page No.
Executive Summary.....	2
1. Introduction.....	3
2. Selection of Materials.....	5
3. Discussion of Results.....	11
4. Summary & Conclusions.....	31
5. References.....	31
Acknowledgements.....	33

## EXECUTIVE SUMMARY

The major objective of this material program is to develop an improved epoxy nanocomposite for carbon fiber-reinforced polymer matrix composite (CPMC) with higher temperature performance capability, mechanical performance, damage resistance, extreme environment corrosion resistance, and improved dimensional control. We proposed that a nanophase be introduced into specific components of an epoxy resin system, prior to cure, to provide improved  $T_g$  and mechanical strength of the composites. In this study, we used Cytec Engineered Materials (CEM) CYCOM® 977-3, a high temperature damage tolerant tetrafunctional epoxy resin system; and three types of nanoparticles: chemically modified montmorillonite (MMT) organoclays, surface treated nanosilica, and surface modified carbon nanofibers (CNF) to create new types of epoxy nanocomposites. Wide angle X-ray diffraction (WAXD) and transmission electron microscopy (TEM) were used to determine the degree of dispersion. Dynamic mechanical thermal analysis (DMTA) was used to determine the  $T_g$  and complex modulus of the polymer nanocomposites.

The TEM analyses indicated that the MMT clay, nanosilica, and CNF dispersed very well in the epoxy resin system. Evidence is presented that a nanophase is formed when nanoparticles such as surface treated clay, surface treated nanosilica, or carbon nanofibers are introduced into the epoxy resin. Higher  $T_g$  and complex modulus values from DMTA for the nanomodified materials are presented as evidence for nanophase presence in the epoxy resin system as compared to lower  $T_g$  and complex modulus for the epoxy resin control. The DMTA data of the neat epoxy nanosilica nanocomposite (2% Aerosil® R202) show the highest  $T_g$  (258°C) and the highest complex modulus (964 MPa).

Five epoxy nanocomposites were selected to produce prepregs using AS4-6K carbon woven cloth at CEM. The prepregs were fabricated into composites. A set of two 18- by 11- by 0.15-inch composite panels were fabricated for physical, thermal, and mechanical properties characterization. Mechanical properties such as  $G_{1C}$ ,  $G_{2C}$ , flatwise tension strength, short beam shear strength, and flexural strength were determined on the epoxy nanocomposites PMCs and compared with the baseline 977-3/AS4-K6 material.

The resulting NCPMC were equal to or better than the baseline 977-3/AS4-K6 in short beam shear, flexural strength, and flatwise tension strength but deficient in  $G_{12}$  and  $G_{2C}$  values.

## 1.0 INTRODUCTION

Carbon fiber-reinforced polymer matrix composites (CPMC) are preferred high performance and advanced composite systems that are utilized in a multitude of applications encompassing aerospace/aircraft structures, advance marine vessels, oilfield drilling risers, fuel cell components, natural gas fuel tanks, sports, satellites and others. These CPMC materials are based on high strength, high  $T_g$  resin systems such as epoxies, BMI, cyanate esters, and polyimides. These resins are well established components within the resulting CPMC that are currently qualified/specified in most of these critical applications. Yet there are occasions when further improvements in CPMC are desired or mandated. Areas of improvement include higher temperature performance capability, mechanical performance, damage resistance, extreme environment corrosion resistance, and improved dimensional control.

In this study, we proposed the use of nanocomposite concepts for improving CPMC and for incorporating within a matrix resin. Subsequently the nanomodified matrix resin is combined with carbon fiber into the resulting nanocomposite CPMC. It is anticipated that nanocomposite CPMC would exhibit many of desired improvements mentioned earlier.

Epoxy resins are one of the matrix resins used in many high performance and advanced carbon fiber composites, CPMC, today. Epoxies possess a combination of characteristics that are outstanding at a reasonable cost. These include a wide choice of forms from low viscosity liquids to solids, a variety of curing systems (amine or anhydride), latitude in processing conditions, low shrinkage, no volatiles emitted, good mechanical properties, good chemical resistance, good adhesion to fiber reinforcement, thermal stability over a wide temperature range, and good resistance to moisture. The ease of epoxy processing in all composite fabrication methods such as prepreg/tape placement, pultrusion, filament winding, SMC, RTM, and hand lay up is also an attractive feature. Limited ductility and reduced hot/wet strength performance are areas requiring improvement and may be enhanced by the development of the nanocomposite phase within the CPMC. Within the family of epoxy resins, there are general purpose and intermediate  $T_g$  ( $<150^\circ\text{C}$ ) epoxies and high performance, high  $T_g$  ( $>200^\circ\text{C}$ ) multifunctional epoxy resins. Of particular importance are the multifunctional epoxy resins that are well established in many aerospace and aircraft CPMC components. These include the trifunctional triglycidyl p-aminophenol (TGAP) and the tetrafunctional tetraglycidyl diamino diphenylmethane (TGDDM) resins. Thus the nanophase modification of these multifunctional epoxy resins contained within the CPMC would generate the desirable improvements.

Modification of epoxy resins through the introduction of a "nanophase" into the uncured epoxy resin composition is proposed by the Koo & Associates International, Inc. (KAI) and The University of Texas at Austin (UT) team as a means of significantly improving the performance characteristics of the CPMC. This will result in an improvement of higher temperature performance capability, mechanical performance, damage resistance, extreme environment corrosion resistance, and improved dimensional control. The presence of "nanophase" in many polymeric systems, either thermoplastic, thermosetting, or thermoplastic elastomer has provided these polymeric materials with substantially improved mechanical properties and performance characteristics as demonstrated by Vaia [1], Giannelis [2], Koo [3-5], Lichtenhan [6], Lake [7], and Gilman [8]. Many different types of nanoparticles have been introduced into epoxy resins resulting in enhanced mechanical properties of the cured epoxy resin systems as demonstrated by Barron [9], Zilg [10], Tie Lan [11], Seferis [12], Bakis [13], Curliss [14-16], Becker [17, 18], Lee [19], and Pittman [20]. Barron [9] has shown that when epoxy is attached to "nanoalumina,"

tensile strength of the epoxy/nanoalumina ranges from 15 to 68 Mpa as compared to 2 Mpa for epoxy control. Higher modulus and tensile strength are reported for nanoclay modified epoxy system using long aliphatic chain imidazoles as the clay surface modifier [10]. Tie Lan *et al.* [11] reported increased  $T_g$  from 120°C to 140°C with a corresponding 10-20% increase in modulus when anhydride cured epoxy resin is modified with nanoclay. Seferis *et al.* [12] have used both alumina nanofibers and alumina nanoparticles to improve lap shear, peel strength, and fracture toughness of epoxy based film adhesives. Single-wall carbon nanotubes (SWNT) were introduced into an epoxy/amine system by Bakis *et al.* [13] for a filament winding application with the anticipation of an increase in compressive strength. No noticeable reinforcing effect (compressive strength) was observed at a 1% SWNT loading. Attempts to introduce 5% SWNT resulted in an unmanageable high viscosity resin system. Chen and Curliss [14-16] have found that nanoclay in an epoxy/amine composition resulted in reduced thermal expansion coefficients, higher dynamic mechanical storage modulus and static modulus with slightly reduced fracture toughness/flexural strength but higher solvent resistance [14]. However when the same nanoclay epoxy amine system was applied to carbon fiber, no significant improvements in mechanical properties were observed [15]. Since neither high shear mixing of nanoclay/resin nor use of added coupling agents (tethering agents) were used by the authors, little benefit occurred with the use of nanoclay. These improved conditions are being contemplated by Chen and Curliss [14-16] for future work. More recently Becker *et al.* [17, 18] have examined amine cured multifunctional epoxy resins, TGAP and TGDDM, with surface modified clay. Improvement in modulus and toughness was observed for these multifunctional cured epoxies; however lower  $T_g$ 's were noted and were caused by lower crosslink density. The authors attributed the lower crosslinking and lower  $T_g$  of the nanoclay epoxy systems to either some epoxy homopolymerization or unreacted resin plasticization.

In virtually all nanomodified epoxy resin systems, enhanced mechanical properties are observed. Yet these results using nanoparticles for increased thermal resistance or increased  $T_g$  are variable. Tie Lan [11] reported higher  $T_g$  values in anhydride cured epoxy when both epoxy components (epoxy resin and anhydride) were intercalated with nanoclay prior to cure. Zilg [10] and Becker [17, 18] intercalated only the epoxy resin with nanoclay and not the amine hardener. Recent studies by Vaia and coworkers [21] indicate that there are subtle considerations in using surface treated clay with each epoxy component, i.e., epoxy resin with clay and amine hardener with clay. These include viscosity increases within each component and then combining these nanoclay modified components for reaction and crosslinking into the cured epoxy. A facile intergallery transfer of epoxy and amine must occur to facilitate cure and obtain the desired nanophase within the cured epoxy. Pinnavaia and coworkers [22-23] have remedied the intercalation/exfoliation of amine hardener by employing a concomitant use of the amine as clay surface modifier and epoxy curing agent.

However the use of the nanomodified epoxy resin systems as matrix resin systems for fiber reinforced composite materials has been a challenge. The introduction of nanoparticles into the epoxy resin system is sensitive to the amount of nanoparticles that are introduced into the epoxy. Resin viscosity increase exponentially as weight per cent of nanoparticles is increased from 1% to 5-7%. With a manageable resin viscosity when 1% of nanoparticle is added, little or no benefit in mechanical properties occurs. Mechanical properties enhancement usually occurs when nanoparticle loadings are 5-7% resulting in excessive resin viscosity behavior and erratic, non-uniform fiber "wet-out" during impregnation of fibers or fabric in the fabrication of the fiber

reinforced composite. The challenge is to lower the viscosity of the nanoparticle/polymer mixture for processing.

Besides the judicious selection of appropriate nanoparticles to substantially improve the properties of the carbon epoxy system, novel high shear processing equipment will be utilized to uniformly disperse nanoparticles into the epoxy resin components. Several viscosity reduction techniques will be examined after the uniformly dispersed nanoparticle epoxy resin system is obtained. Techniques to be used include modest temperature increase, low viscosity reactive diluents functioning as coupling agents (tethering agents), or volatile solvent [21] which is removed during impregnation of fiber/fabric. These viscosity reduction techniques will be monitored by rheology to determine optimum viscosity reduction versus resin out time.

The major objective of this material program is to develop an improved nanocomposite carbon fiber-reinforced polymer matrix composite with enhanced mechanical properties. We proposed that a nanophase be introduced into the multi-functional epoxy resin system, prior to cure, to provide improved and maintained mechanical strength of the composites. In this study, we used (a) Cytec Engineered Material's tetrafunctional epoxy system; (b) *three types of nanoparticles*: chemically modified montmorillonite (MMT) organoclays, nanosilica, and carbon nanofibers (CNF) to create new types of nanocomposite carbon fiber-reinforced polymer matrix composites (NCPMC).

The minor objectives of this investigation are to: (a) develop processes to disperse these nanoparticles uniformly in the epoxy resin prior to curing, (b) use wide-angle X-ray diffraction (WAXD), transmission electron microscopy (TEM), and scanning electron microscopy (SEM) to characterize polymer nanocomposite morphological behavior after curing, (c) study structure-property relationship of these types of new materials, (d) study the rheology of the polymer nanocomposites, and (e) evaluate the performance (mechanical properties) of these carbon fiber-reinforced composites.

Five resin/nanoparticle material systems were selected to produce carbon fiber-reinforced prepregs at Cytec Engineered Materials. The prepregs were produced using AS4-6K woven cloth [in a 5-harness satin weave with a nominal (wrap) x 11 (fill) construction with areal weight of 356-384 g/m<sup>2</sup>]. Polymer matrix composites were fabricated using CEM's proprietary procedures for the five candidates and the baseline 977-3/AS4-6K materials. Mechanical properties such as G<sub>1C</sub>, G<sub>2C</sub>, FWT, SBS, and flexural strength were determined on these nanomaterials and are compared with the baseline 977-3 material.

## 2. SELECTION OF MATERIALS

**2.1 Resin Systems** Polymer system is an important component of the CPMC materials. CYCOM® 977-3 toughened epoxy resin was selected for this study, since this is an industry standard recommended by Cytec Engineered Materials [24]. CYCOM® 977-3 [24] is a 350°F (177°C) curing toughened epoxy resin with a 350°F (177°C) dry and 270°F (132°C) wet service capability. CYCOM® 977-3 is formulated for autoclave or press molding and can be cured at 350°F (177°C) for six hours. Unidirectional tape and woven fabric impregnated with CYCOM® 977-3 resin will retain tack for 30 days at 72°F (22°C) and has a long mechanical outlife suitable for fabrication of large structures. Typical applications for CYCOM® 977-3 include aircraft primary and secondary structure or any application where impact resistance and excellent hot/wet performance are crucial. Below are several features and benefits of CYCOM® 977-3:

- Toughened epoxy using CEM's proprietary "co-continuous" morphology
- Superior hot/wet performance with impact resistance
- 350°F (177°C) cure
- Available in broad range of fibers and forms including tape, fabric, and roving
- 350°F (177°C) dry and 270°F (132°C) wet service temperature
- Autoclave or press-mold processing
- Shelf life 6 months at 0°F (-18°C) or 30 days at 72°F (22°C)

Typical cured neat resin and composite laminates properties of CYCOM® 977-3 are shown in Tables 1 and 2, respectively [24].

**Table 1** Cured<sup>1</sup> Neat Resin Properties of CYCOM® 977-3 [24]

Property	RT	250°F(121°C)/Wet <sup>2</sup>
Compressive Yield Strength, ksi (MPa)	27.0 ± 0.3 (186 ± 2.1)	
Flexural Strength <sup>3</sup> , ksi (MPa)	21.0 ± 4.4 (144.7 ± 30.3)	10.14 ± 0.4 (69.9 ± 2.8)
Flexural Modulus <sup>3</sup> , Msi (GPa)	0.55 ± 0.01 (3.79 ± 0.07)	0.354 ± 0.3 (2.41 ± 2.1)
K <sub>IC</sub> <sup>4</sup> , (MPa). m <sup>1/2</sup>	0.90 ± 0.08	
G <sub>IC</sub> <sup>4</sup> , (J/m <sup>2</sup> )	217 ± 24	
RDS DMTA T <sub>g</sub> , °C (tested @ 5°C/min) G'		178,218
G''		189,226
Tan Delta		190,240

<sup>1</sup> Cured at 350°F (180°C) for 6 hours.

<sup>2</sup> Wet = 7-day water immersion at 160°F (71°C).

<sup>3</sup> Flexural testing performed using a 3-point loading fixture and a 16:1 S/D ratio.

<sup>4</sup> K<sub>IC</sub> and G<sub>IC</sub> tested using 3-point bending mode.

**2.2 Polymer Nanoparticles** Three types of nanoparticles were used in this Phase I study, namely Southern Clay Products' montmorillonite nanoclays (MMT nanoclays), Applied Sciences' carbon nanofibers (CNF), and Degussa' nanosilica materials. Hybrid Plastics' Polyhedral Oligomeric Silsesquioxanes (POSS®) materials, MER Corp.'s multi-wall carbon nanotubes (MWNT) and Carbon Nanotechnologies' single-wall carbon nanotubes (SWNT) are good candidates, however due to their costs they will not be included in the Phase I, but will be considered in the Phase II study. These nanoparticles will reinforce the polymer in the nanoscale and will enhance the dimensional stability and mechanical properties of the polymer nanocomposites [1-23]. To achieve the potential improvements nanoparticles usually require some degree of dispersion and exfoliation (for MMT nanoclays). These are shown to be dependent upon a combination of proper chemical treatment and optimized processing.

**Montmorillonite Nanoclays** - Exfoliation of montmorillonite (MMT) clays into polymer will increase mechanical properties, barrier performance, and application processing [25]. Koo *et al.* [3, 4] are currently using the phenolic resole resin (SC-1008) with organomontmorillonite Cloisite® 30B and 10A and have observed intercalation and not exfoliation based on XRD and TEM analyses on high clay loading [3, 4]. The nanoclay also enhanced ablation, heat transfer, and flammability characteristics of the ablative materials [4].

Table 2 Typical Properties of CYCOM® 977-3 Laminates [24]

Typical properties of 977-3 composite laminates

INTERMEDIATE MODULUS (40 Msi/276 GPa CLASS)  
CARBON FIBER REINFORCED UNIDIRECTIONAL TAPE

Typical CEM Product Codes

Hy-E 1377-3T; Hy-E 5377-3A; Hy-E 1577-3E

Mechanical Properties	-75°F	RT	220°F		250°F		270°F		300°F	
			Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
<b>0° Tensile Properties</b>										
Strength, ksi	353	364								
Modulus, Msi	22.9	23.5								
Strain, %	1.52	1.46								
<b>90° Tensile Properties</b>										
Strength, ksi		9.3								
Modulus, Msi		1.21								
Strain, %		0.77								
<b>0° Compressive Properties</b>										
Strength, ksi		244		221 <sup>1</sup>		195 <sup>1</sup>		180 <sup>1</sup>		160 <sup>1</sup>
Modulus, Msi		22.3	21.4	21.2 <sup>1</sup>	20.4	21.2 <sup>1</sup>	20.2	22.6 <sup>1</sup>	21.5	21.7 <sup>1</sup>
<b>Open Hole Compression</b>										
Strength, ksi (25/50/25 orientation)		46.7		37.0 <sup>2</sup>		35.0 <sup>2</sup>				
<b>0° Interlaminar Shear Properties</b>										
Strength, ksi		18.5	13.6	12.9 <sup>1</sup>	13.3	11.4 <sup>1</sup>	12.4	10.1 <sup>1</sup>	11.4	9.0 <sup>1</sup>
<b>In-Plane Shear Properties (+45)</b>										
Modulus, Msi		0.72		0.61 <sup>3</sup>		0.58 <sup>3</sup>		0.50 <sup>3</sup>		0.34 <sup>3</sup>
Weight Gain = 0.9%										
<b>0° Flexural Properties</b>										
Strength, ksi		256	246	173 <sup>1</sup>	221	162 <sup>1</sup>	218	140 <sup>1</sup>	206	125 <sup>1</sup>
Modulus, Msi		21.7	22.2	20.1 <sup>1</sup>	20.8	21.2 <sup>1</sup>	21.0	19.6	21.0	18.9
<b>90° Flexural Properties</b>										
Strength, ksi		19.0								
Modulus, Msi		1.19								
<b>Edge Delamination Strength, ksi</b>										
Onset		37								
Ultimate		92								
<b>Compression After Impact, ksi</b> (25/50/25 orientation 270 in-lb impact level)		28								
<b>Interlaminar Fracture Toughness</b>										
G <sub>IC</sub> (DCB), in-lb/in		1.8								
G <sub>IE</sub> (ENF), in-lb/in		3.3								

NOTES:

All panels cured for 6 hours at 355°F, 85 psi

<sup>1</sup>Wet = 1 week Immersion in 160°F water

<sup>2</sup>Wet = 2 week Immersion in 160°F water

<sup>3</sup>Wet = 150°F/85% RH to equilibrium  
(approximately 1.1% weight gain)

The data listed has been obtained from carefully controlled samples considered to be representative of the product described. Because the properties of this product can be significantly affected by the fabrication and testing techniques employed and since Cytec Engineered Materials does not control the conditions under which its products are tested and used, Cytec Engineered Materials cannot guarantee that the properties listed will be obtained with other processes and equipment.



Achieving exfoliation of organomontmorillonite in various continuous phases is a function of the surface treatment of the MMT clays and the mixing efficiency of the dispersing protocol. Surface treatment of MMT is classically accomplished with the exchange of inorganic counterions, e.g. sodium, etc., with quaternary ammonium ions. The choice of the quaternary ammonium ion is a function of the hydrophilic/hydrophobic nature of the continuous phase; the hydrophilic/hydrophobic nature of the interface of MMT is balanced with the hydrophobic/hydrophilic nature of the continuous phase. The continuous phase, in this case, is epoxy resin. Mixing efficiency, in the epoxy was achieved with standard paint mixing equipment [3, 4].

The Cloisite® 30B is a natural montmorillonite manufactured by SCP [26]. It is an additive for plastics to improve various plastic physical properties, such as reinforcement, heat distortion temperature, and barrier. It has ternary ammonium salt modifier at 90 meq/100g clay and is off white in color. Its typical dry particle size and physical properties are shown in Tables 3 and 4, respectively. Cloisite® 30B in loadings of 5, 10, 15, and 20 wt.-% were dispersed in a phenolic resole (SC-1008) by Koo *et al.* [4].

The Cloisite® 10A is a natural montmorillonite manufactured by SCP [27]. It is an additive for plastics to improve various plastic physical properties. It has quaternary ammonium salt modifier at 125 meq/100g clay and is off-white in color. Its typical dry particle size and physical properties are shown in Tables 3 and 4, respectively.

**Table 3** Typical Dry Particle Sizes for Cloisite® 30B and 10A (Microns, by Volume)

10% LESS THAN	50% LESS THAN	90% LESS THAN
2 $\mu$	6 $\mu$	13 $\mu$

**Table 4** Physical Properties of Cloisite® 30B and 10A (Microns, by Volume)

PROPERTY	CLOISITE® 30B	CLOISITE® 10A
Loose bulk density, lb/ft <sup>3</sup>	14.25	10.21
Packed bulk density, lb/ft <sup>3</sup>	22.71	16.52
Specific gravity	1.98	1.90
d <sub>001</sub> , Å	18.5	19.2

**Carbon Nanofibers (CNF)** – CNF are a form of vapor grown carbon fiber, which is a discontinuous graphitic filament produced in the gas phase from the pyrolysis of hydrocarbons [28-31]. In properties of physical size, performance improvement, and product cost, CNF completes a continuum bounded by carbon black, fullerenes, and single-wall to multi-wall carbon nanotubes on one end and continuous carbon fiber on the other [31]. CNF are able to combine many of the advantages of these other forms of carbon for reinforcement in engineered polymers. The CNF have transport and mechanical properties that approach the theoretical values of single crystal graphite, similar to the fullerenes, but can be made in high volumes at low cost - ultimately lower than conventional carbon fibers. In equivalent production volumes, CNF is projected to have a cost comparable to E-glass on a per-pound basis, yet possess

properties which far exceed those of glass and are equal to, or exceed those of much more costly commercial carbon fiber. Maruyama and Alam published an excellent review of carbon nanotubes and nanofibers in composite materials [31].

Carbon nanofibers (CNF) are manufactured by Applied Sciences Inc./Pyrograf® Products by pyrolytic decomposition of methane in the presence of iron-based catalyst particles at temperatures above 900°C. Pyrograf®-III is a patented, very fine, highly graphitic, carbon nanofiber. Pyrograf®-III is available in diameters ranging from 65 to 200 nm and a length of 50-100  $\mu\text{m}$ . Therefore, CNF are much smaller than conventional continuous or milled carbon fibers (5-10  $\mu\text{m}$ ) but significantly larger than carbon nanotubes (1-10 nm). Compared to PAN and pitch-based carbon fiber, the morphology of CNF is unique in that there are far less impurities in the filament, providing for graphitic and turbostratic graphite structures, and the graphene planes are more preferentially oriented around the axis of the fiber. Consequences of the circumferential orientation of high purity graphene planes are a lack of cross-linking between the graphene layers, and a relative lack of active sites on the fiber surface, making it more resistant to oxidation, and less reactive for bonding to matrix materials. Also in contrast to carbon fiber derived from PAN or pitch precursors, CNF is produced only in a discontinuous form, where the length of the fiber can be varied from about 100  $\mu\text{m}$  to several cm, and the diameter is of the order of 100 nm.

Carbon nanofibers have exceptional mechanical and transport properties, giving them excellent potential as an engineering material. Table 5 lists the properties of vapor-grown carbon fibers, both as grown, and after a graphitizing heat treatment to 3000°C. Note that, due to the difficulty of direct measurements on the nanofibers, the values in Table 5 are measured on vapor-grown fibers that have been thickened to several microns in diameter [30]. Such fibers consist almost exclusively of CVD carbon, which is less graphitic and more defective than the catalytically grown carbon core that constitutes the carbon nanofiber. Thus the properties listed in the table represent an estimate for the properties of nanofibers.

**Table 5** Properties of Carbon Nanofibers [30]

Property (Units)	As Grown	Heat Treated
Tensile Strength (GPa)	2.7	7.0
Tensile Modulus (GPa)	400	600
Ultimate Strain (%)	1.5	0.5
Density (g/cc)	1.8	2.1
Electrical Resistivity ( $\mu\Omega\text{-cm}$ )	1000	55
Thermal Conductivity (W/m-K)	20	1950

One of the goals for CNF application is to provide mechanical reinforcement comparable to that achieved with continuous tow carbon fiber at a price that approaches that of glass fiber reinforcement, and with low cost composite fabrication methods such as injection molding. Theoretical models [30] suggest that reinforcement by discontinuous fibers, such as the CNF, can closely approach that of continuous fibers as long as the aspect ratio of the fibers is high and the alignment is good. Work is ongoing to improve the mechanical benefits of CNF through fiber surface modification to provide physical or chemical bonding to the matrix. Such modifications have resulted in strength and modulus improvements of 4 to 6 times the values of

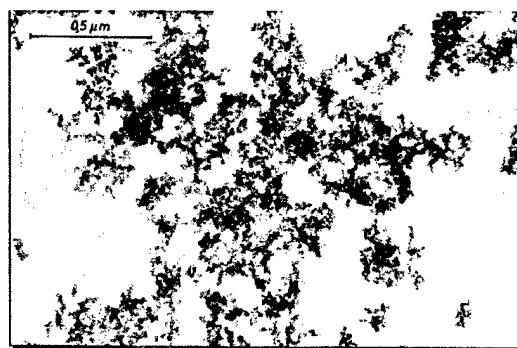
the neat resin; however, these values are still a modest fraction of what may be anticipated from idealized fiber/matrix interphase and alignment of the fibers within the matrix. The more immediate opportunities for application in structural composites lie in the prospect for modifying the properties of the matrix material. For example, use of small volume loadings in epoxy may allow for improvement of interlaminar shear strength of PAN or pitch-based composites. CNF additives to fiberglass composites could provide benefits to a suite of properties, including thermal and electrical conductivity, coefficient of thermal expansion, and mechanical properties, as suggested by the data in Table 6 [30]. Carbon nanofibers will be functionalized with amine functionality [32] on the surface and will result in co-reaction with the epoxy resin leading to improved interfacial adhesion between the epoxy resin and the carbon nanofiber.

**Table 6** Thermoset Polyester/Pyrograf®-III Composite Properties

Fiber Content (Wt. %)	Tensile Strength (MPa)	Tensile Modulus (GPa)	Electrical Resistivity (ohm-cm)
17% PR-19	51.5	4.55	3.2
17% PR-19, OX	47.4	4.55	7.1
5% PR-19 in 10% ¼" glass	44.1	11.52	5.0
5% PR-19, OX in 10% ¼" glass	33.8	8.92	7.0

**Nanosilica** – AEROSIL is highly dispersed, amorphous, very pure silica which is produced by high temperature hydrolysis of silicon tetrachloride in an oxyhydrogen gas flame [33-35]. The primary particles are spherical and free of pores. The primary particles in the flame interact to develop aggregates which join together reversibly to form agglomerates. Figure 9 shows a TEM micrograph of AEROSIL® 300 in which the primary particles, aggregates and agglomerates can be clearly seen [33]. The average diameters of the primary particles are in the range of 7 to 40 nm according to the AEROSIL grade. The specific surface areas range between 50 to 380 m<sup>2</sup>/g. Siloxane and silanol groups are situated on the surface of the AEROSIL particles. The latter is responsible for the hydrophilic behavior of the untreated AEROSIL. Hydrophilic and hydrophobic grades of AEROSIL have proved successful for use in numerous applications. They can be used as reinforcing filler, thickening and thixotropic agent, anti-settling agent, and free-flow aid.

AEROSIL® is a submicron amorphous silica which has been used successfully for decades as a thickening agent and thixotrope in liquid system. It is also used to adjust the rheological properties of epoxy resins. We selected two new Degussa products for this investigation. They are the hydrophobic AEROSIL® R202 and AEROSIL® R805 materials. They also serve as rheological aids to provide effective, stable thickening and thixotropy of epoxy systems [33-35]. AEROSIL® fumed silica for rheology control is widely used in silicone rubber, coatings, plastics, printing inks, adhesives, lubricants, creams, ointment, and in toothpaste. Nelson and co-workers used this nanoparticle with polystyrene in their recent study demonstrating significant improvement in reduced flammability [36]. AEROSIL® R202 [35] is a fumed silica treated with a polydimethylsiloxane. AEROSIL® R805 [34] is a fumed silica treated with an octylsilane based on AEROSIL® 200. Typical properties of AEROSIL® R805 and R202 are listed in Table 7.



**Figure 1** TEM micrograph of AEROSIL® 300 [33].

**Table 7** Material Properties of AEROSIL® R805 and R 202 [34, 35]

PROPERTIES	AEROSIL® R 805	AEROSIL® R 202
Specific surface area (BET) (m <sup>2</sup> /g)	150 ± 25	100 ± 20
Carbon content (%)	4.5 – 6.5	3.5 – 5.0
Average primary particle size (nm)	12	14
Tapped density standard material (g/l)	50	50
Moisture 2 hours at 105°C	<0.5	<0.5
Ignition loss 2 hours at 1,000°C based on material dried for 2 hours at 105°C	5.0 – 7.0	4.0 – 6.0
pH value in 4% dispersion	3.5 – 5.5	4.0 – 6.0
SiO <sub>2</sub> – content based on ignited material (%)	>99.8	>99.8

### 3. DISCUSSION OF RESULTS

The candidate materials developed are screened for dispersion using WAXD and TEM prior to full scale up. Lab scale dispersion of specific components of the 977-3 resin system with different wt% nanoclays, CNF, and nanosilica were conducted as shown in Table 8. The morphology of selective resin/nanoparticle systems were characterized using WAXD, TEM and SEM analyses. Mixing procedures are designed to achieve full contact between the nanoparticles and the polymer matrix. There are two basic types of nanoparticles for this study: carbon nanofibers and particulate solids like the nanoclays and nanosilicas. In all cases, the mixing procedure must allow sufficient opportunity for the liquid monomers to contact and fully wet out the surface of the nanoparticles.

The silicas have a very convoluted, high surface area and need a long contact time in a low viscosity medium to fully wet out their surface. The clays also require a substantial residence time to allow the matrix monomers to penetrate the layers of the clay and fully exfoliate the layered structure. Clays and silicas are used as-received condition with no additional preparation. The CNFs are highly entangled and also require a long contact time to wet out their surfaces. CNF's are first screened through a 100 mesh screen to break down any large clusters of the CNF. At 100 mesh, the aspect ratio of the CNF will still be greater than 1,000:1. Mixing

and curing procedures were developed for the preparation of the nanocomposites based on the mixing profile originally provided by CEM. Nanoparticles are added after the liquid components of the 977-3 resin are mixed. A 30 minute hold at that point allows the various solids to wet out and disperse. Samples were made for TEM and DMTA analyses.

**Table 8** Blending Matrix for 977-3/Nanoparticle Resin Systems

CANDIDATE NO.	EPOXY COMPONENT OF 977-3 SYSTEM (WT PERCENT)	NANOPARTICLES (WT PERCENT)	NANOPARTICLES TYPE
1	100%	0%	None
2	99%	1%	Cloisite® 30B
3	98%	2%	Cloisite® 30B
4	95%	5%	Cloisite® 30B
5	99%	1%	Cloisite® 10A
6	98%	2%	Cloisite® 10A
7	95%	5%	Cloisite® 10A
8	99%	1%	PR-19-PS amine treated CNF
9	98%	2%	PR-19-PS amine treated CNF
10	99%	1%	PR-19-PS CNF
11	98%	2%	PR-19-PS CNF
12	95%	5%	PR-19-PS CNF
13	99%	1%	PR-19-PS-Ox CNF
14	98%	2%	PR-19-PS-Ox CNF
15	95%	5%	PR-19-PS-Ox CNF
16	99%	1%	AEROSIL® R202
17	98%	2%	AEROSIL® R202
18	95%	5%	AEROSIL® R202
19	99%	1%	AEROSIL® R805
20	98%	2%	AEROSIL® R805
21	95%	5%	AEROSIL® R805

All mixing was carried out in a liquid phase before polymerization. Polymerization was conducted as a separate step in a circulating air oven. Fully cured (polymerized) samples were prepared for DMTA and TEM analyses. The TEM analyses were conducted on selective specimens. These TEM images facilitated screening various formulations for desirable nano-level dispersion of the clay or CNF or nanosilica within the cure resin/inorganic composites. Desirable features included higher levels of clay exfoliation, and uniform dispersion of CNF or nanosilica within the resin both before and after curing.

**3.1 Mixing and Curing Procedures** The *mixing procedure* was modified from that provided by CEM to accommodate available mixing equipment. Formulations were prepared in batches of 200 g in a water jacketed, stirred glass reaction vessel. The 977-3 epoxy resin system consists of four components. Component A and component B of the 977-3 resin system were added to the reaction vessel and stirred for approximately 30 min. at 60°C. After 30 min., the nanoparticles were added and the mixture was stirred for another 30 min. Component C was then added and

the mixture was stirred for another 30 min. as the temperature of the water jacket was increased to 70°C. Component D was then added and the mixture was stirred for another 60 min. The completed mixture was poured onto a Teflon coated sheet for curing. The mixture was several mm thick to allow samples to be cut for DMTA testing. All nanoparticles seemed to wet well with the two monomers (components A and B). Most of the mixtures were viscous liquids at the 1% and 2% modifier content. At 5%, the CNF and Cloisite® 10A mixtures were gel-like and did not flow under their own weight at room temperature.

The *curing procedure* was developed for the nanomodified epoxy resin system. The 977-3 resin system cures over a temperature range approximately 100° to 180°C. CEM recommended a cure cycle that starts at room temperature and ramps up to 180°C (355°F) at a rate of 1 to 5 °F/min. The cure cycle then requires that the mixture be held at 180°C (355°F) for 6 hrs. in order to complete the cure. The temperature is then lowered to room temperature at a rate of about 5°F/min.

This procedure was first applied to the neat, unmodified 977-3 resin. Curing was carried out in a circulating air oven. The sample rapidly discolored and decomposed at a temperature about 150°C (302°F). Apparently in thick specimens, auto catalytic accelerated cure results in a runaway polymerization.

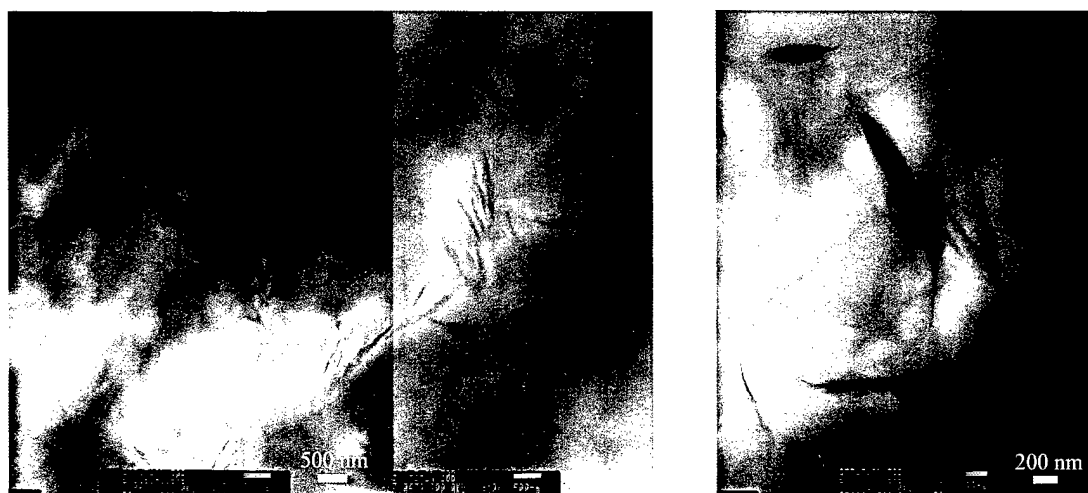
After consulting with CEM, an alternate cure cycle was applied using an intermediate temperature profile to cure the specimens. An intermediate hold of 2 hrs. at 140°C (284°F) was recommended to avoid the auto catalytic accelerated cure problem. A slower ramp to the final cure temperature was also recommended. This resolved the situation and was used with all formulations. The resulting cure profile was developed:

- a. Heat from room temperature to 140°C over 2 hrs. (0.8 °C/min.)
- b. Hold at 140°C for 2 hrs.
- c. Heat from 140°C to 180°C over 2 hrs. (0.3 °C/min.)
- d. Hold at 180°C for 6 hrs.
- e. Cool from 180°C to room temperature over 2 hrs. (1.2 °C/min)

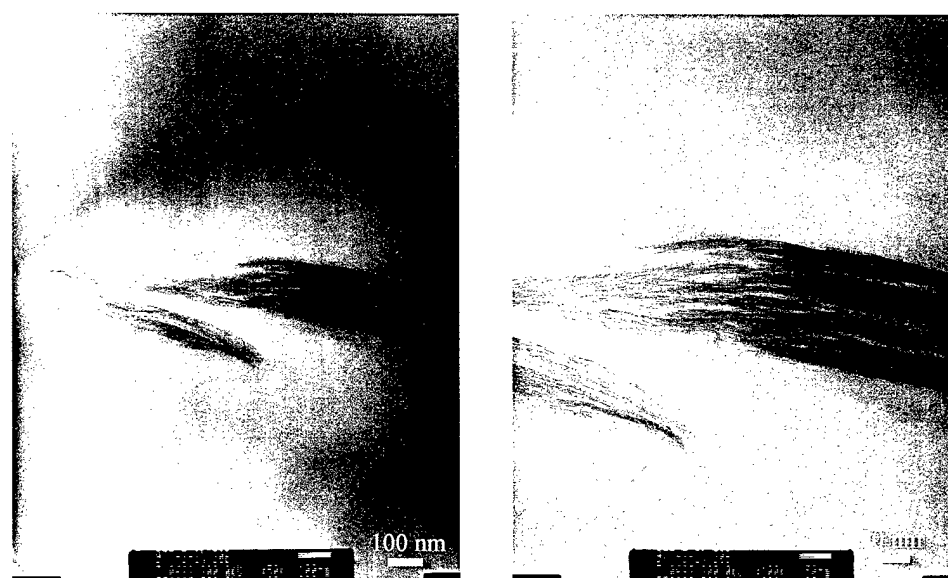
Air bubbles were noted in most of the samples following cure. This might have been mitigated by vacuum bagging or otherwise degassing the mixture.

In summary, the mixing procedures developed provided a simple, reproducible system for preparing the 977-3 epoxy resin system modified with nanoparticles. The low molecular weight monomers seemed to wet out the various nanoparticles and give well dispersed mixtures. The cure procedure gave consistent, solid samples for TEM and DMTA analyses.

**3.2 Processing and Characterization of 977-3/Nanoclay Systems** Weight percent (wt%) of (99/1), (98/2), and (95/5) of Cloisite® 30B and (99/1), (98/2), and (95/5) of Cloisite® 10A nanoclays were blended with specific components of the 977-3 resin system using the mixing procedures developed for this study. Appearance in terms of transparency, translucency, or opaqueness was examined during mixing, before and after curing for all blends. TEM analyses were conducted on selective formulations as shown in Figures 2 through 4 for 977-3/Cloisite® 30B and Figures 5 through 8 for 977-3/Cloisite® 10A.



**Figure 2** Low magnification TEM micrographs of 977-3/Cloisite® 30B (98/2) showing uniform dispersion of Cloisite® 30B nanoclay in the 977-3 epoxy resin where scale bar is 500 nm (left) and 200 nm (right)



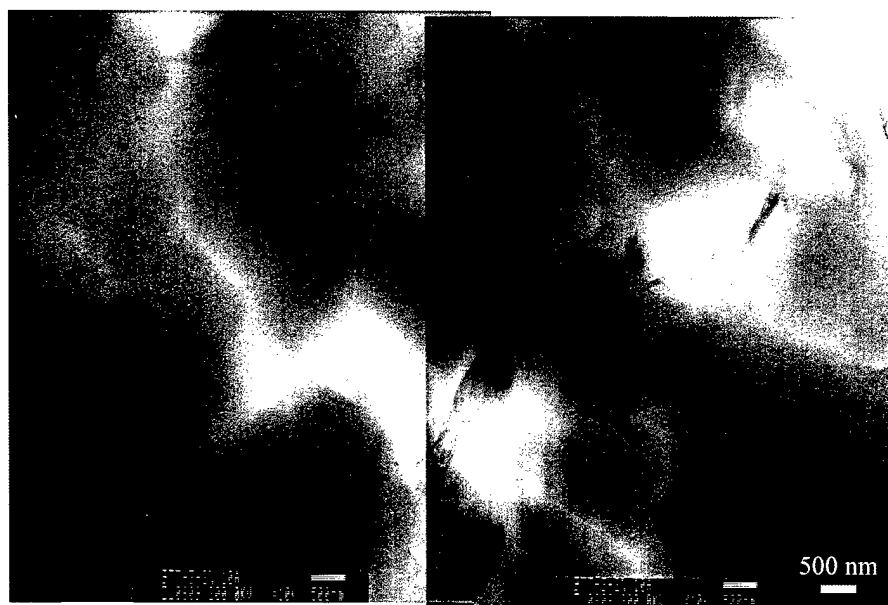
**Figure 3** Higher magnification of 977-3/Cloisite® 30B (98/2) showing nanoclay in an intercalated state in the 977-3 epoxy resin where scale bars are 100 nm (left) and 50 nm (right)

Figure 2 shows the TEM micrographs of uniform distribution of Cloisite® 30B nanoparticles in the 977-3 resin system in (98/2) wt ratio. Figure 3 shows high magnification TEM micrographs showing the Cloisite® 30 clay in an intercalated state in the 977-3 epoxy resin system. Figure 4 shows a progressive state of the 977-3/Cloisite® 30B in (95/5) composition. Figure 5 shows a low magnification of 977-3/Cloisite® 10A in (98/2) composition. Figure 6 shows a high magnification of 977-3/Cloisite® 10A showing the nanoclay in an intercalated state in the 977-3 epoxy resin. Figure 7 shows a low magnification of 977-3/Cloisite® 10A. Both surface treated clays dispersed very well in the epoxy composition as shown in the TEM micrographs. In some cases particularly in Cloisite® 10A, a modest amount of cluster of clays is shown in Figure 6.





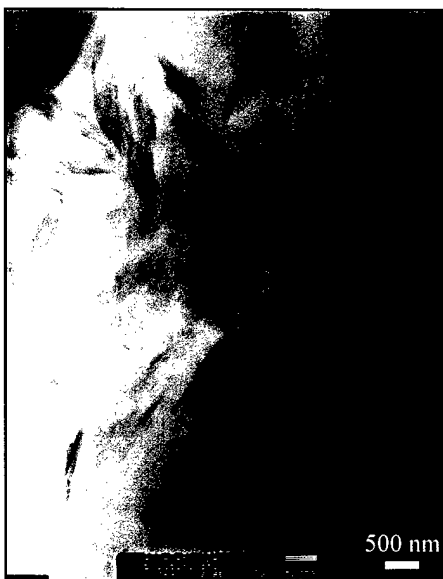
**Figure 4** Higher magnification of 977-3/Cloisite® 30B (95/5) showing nanoclay in an intercalated state in the 977-3 epoxy resin where scale bars are 200 nm (left) and 100 nm (right)



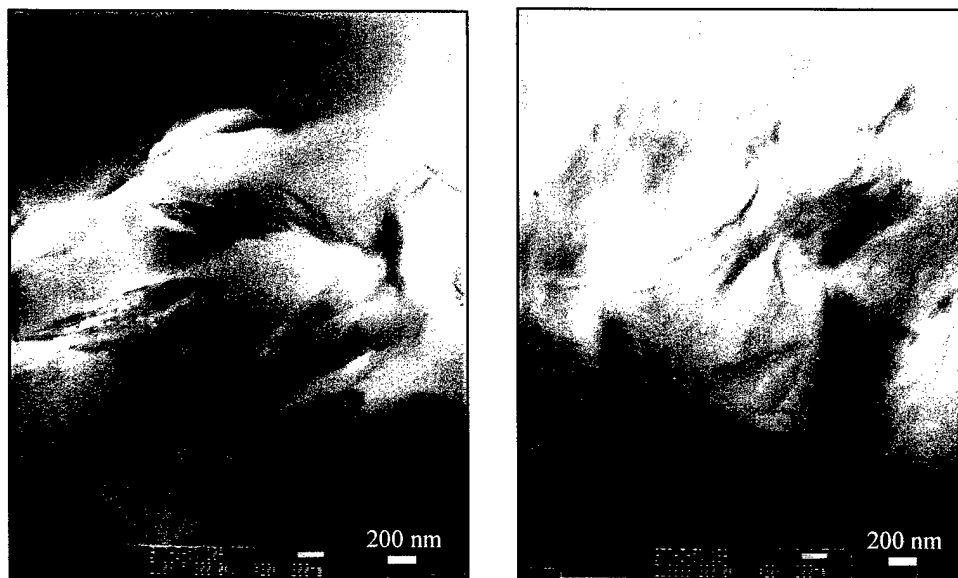
**Figure 5** Low magnification TEM micrographs of 977-3/Cloisite® 10A (98/2) showing uniform dispersion of nanoclay Cloisite® 10A in 977-3 epoxy resin where scale bar is 500 nm



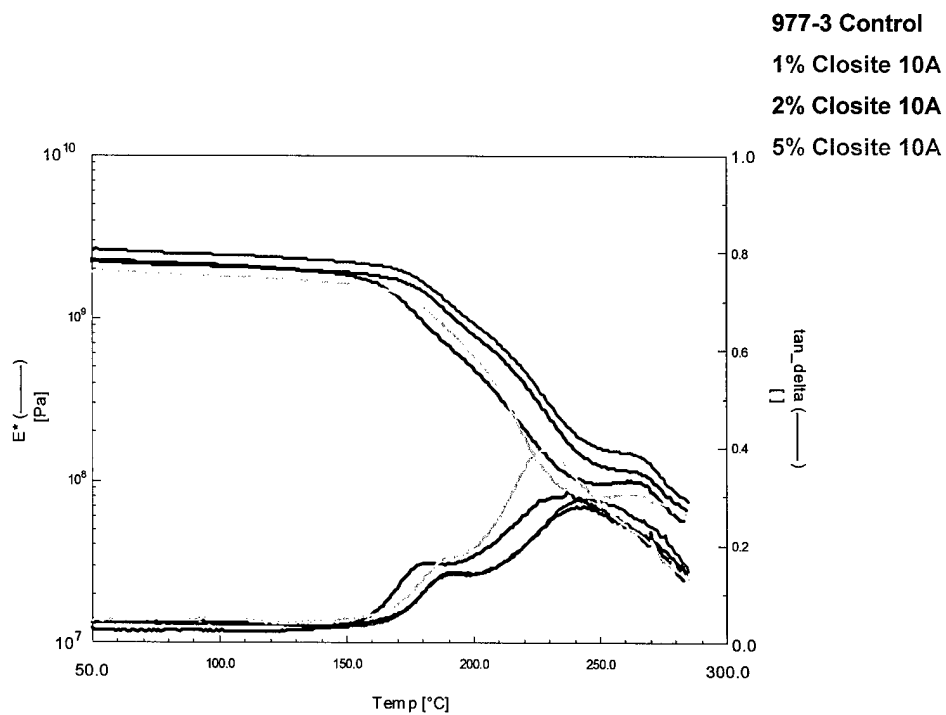
**Figure 6** High magnification TEM micrographs of 977-3/Cloisite® 10A (98/2)



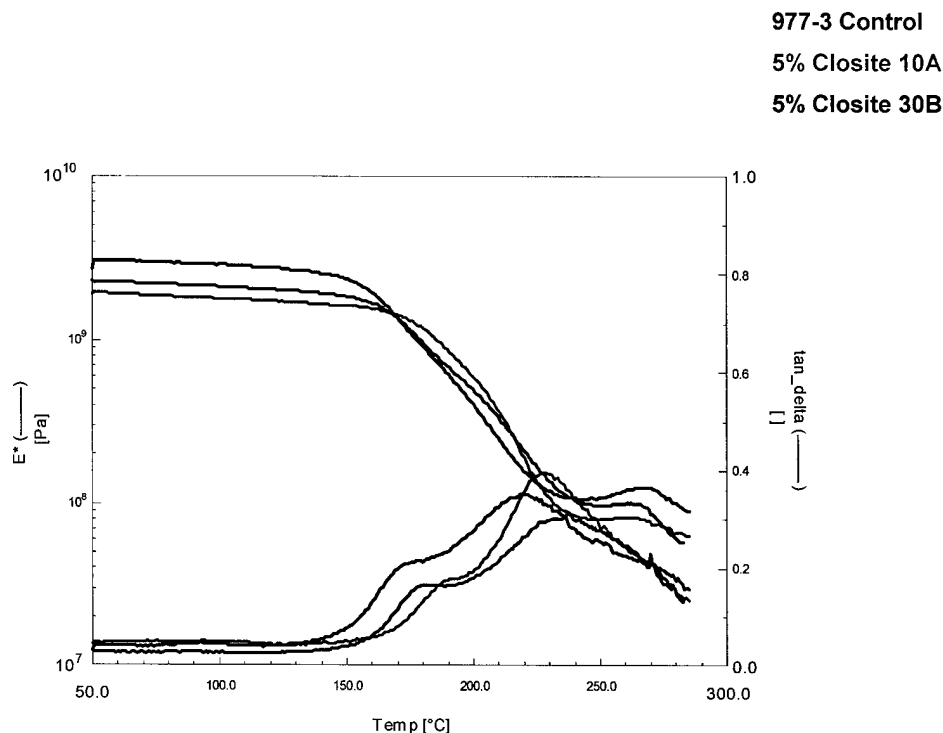
**Figure 7** Low magnification TEM micrographs of 977-3/Cloisite® 10A (95/5) showing uniform dispersion of nanoclay Cloisite® 10A in 977-3 epoxy resin where scale bar is 500 nm



**Figure 8** TEM micrographs of 977-3/Cloisite® 10A (95/5) showing uniform dispersion of nanoclay Cloisite® 10A in 977-3 epoxy resin where scale bar is 200 nm



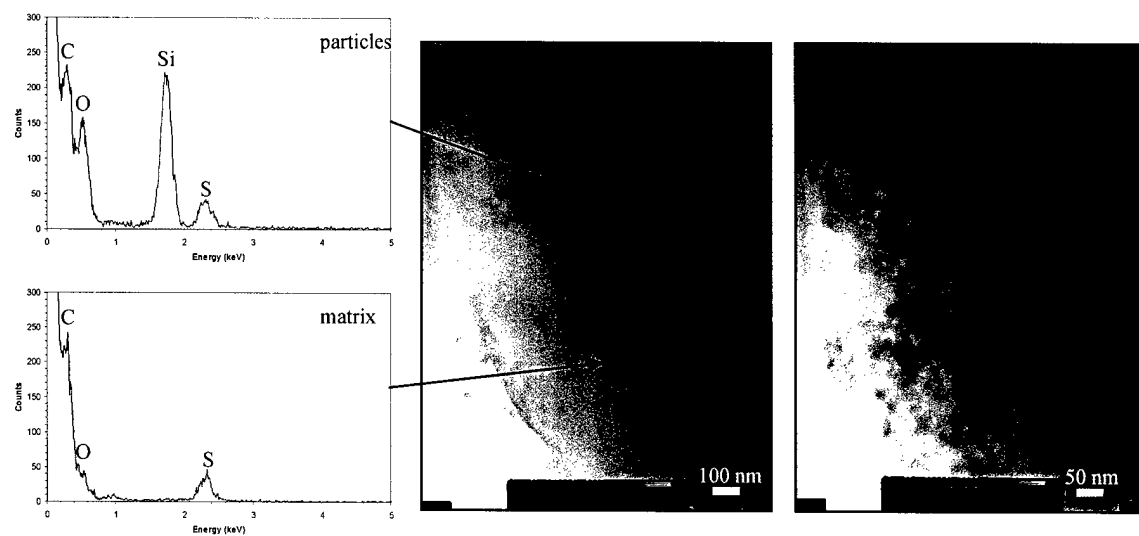
**Figure 9** DMTA analyses of 1%, 2%, and 5 % of Cloisite® 10A in 977-3 epoxy resin



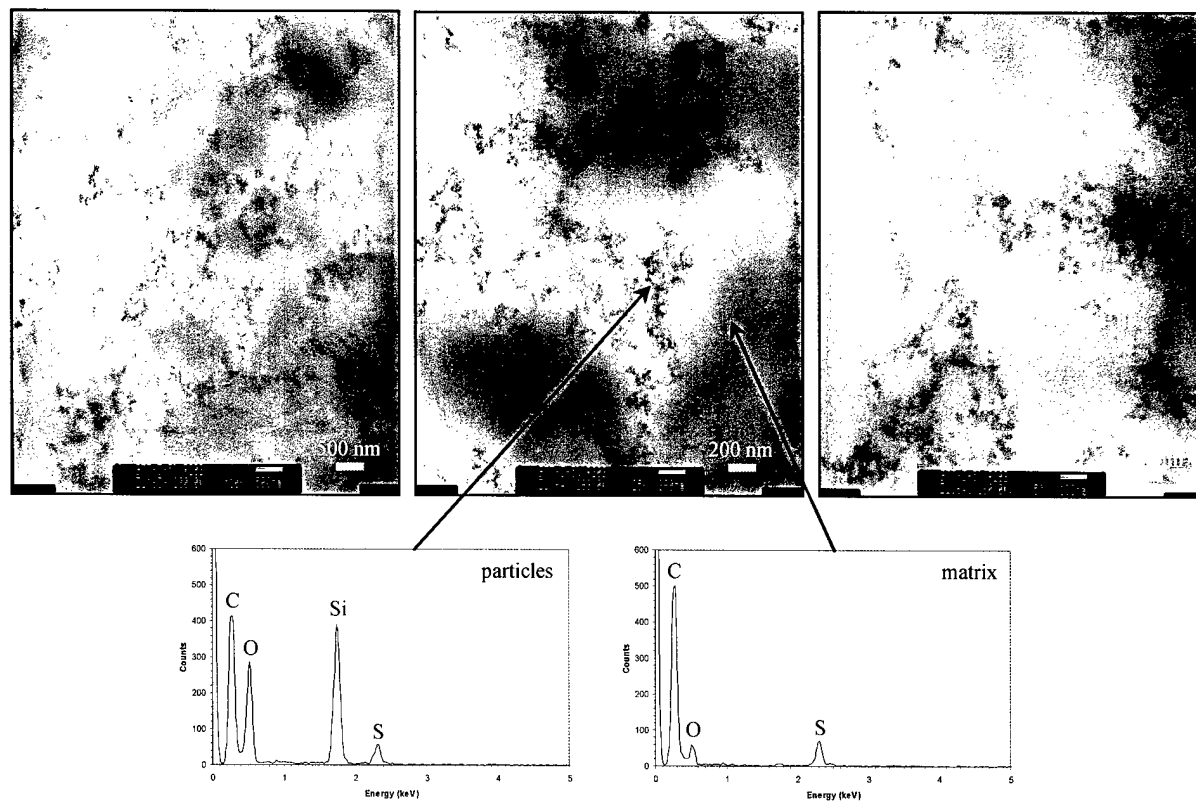
**Figure 10** DMTA analyses of 5 % Cloisite® 10A and 5% Cloisite® 30B in 977-3 epoxy resin

Figure 9 shows a comparison of the DMTA analyses of 1%, 2%, and 5 % Cloisite 10A. At low loading of Cloisite® 10A (1%) increase complex modulus and  $T_g$  were noted. Figure 10 shows the comparison of the 5 % Cloisite® 10A and 5% Cloisite® 30B with Cloisite® 10A providing better performance than Cloisite® 30B.

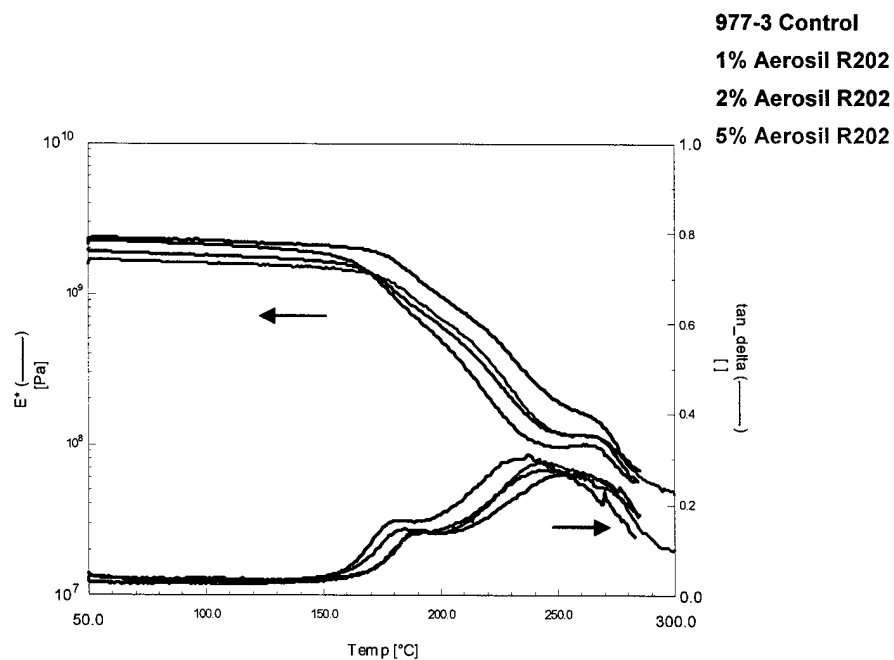
**3.3 Processing and Characterization of 977-3/Nanosilica Systems** The 977-3 was blended with (99/1), (98/2), and (95/5) of Aerosil® R202 and (99/1), (98/2), and (95/5) of Aerosil® R805 using the mixing procedures developed for this study and 6 blends were recorded. Figures 11 and 12 show the TEM micrographs of 977-3 epoxy with 2% and 5 % of Aerosil® R202 nanosilicas. DMTA data (Figure 13) shown the highest  $T_g$  (258°C) and the highest complex modulus (964MPa) for 2% Aerosil® R202. Figures 14 and 15 show the TEM micrographs of 977-3 epoxy with 2%, and 5 % of Aerosil® R805 nanosilicas. The DMTA data (Figure 16) for Aerosil® R805 indicated that a small increase in  $T_g$  and complex modulus is observed but not as effective as Aerosil® R202. It is possible that surface treatment of the R805 by octylsilane resulted in more effective hydrophobic nanosilica and reduced interaction with epoxy monomer.



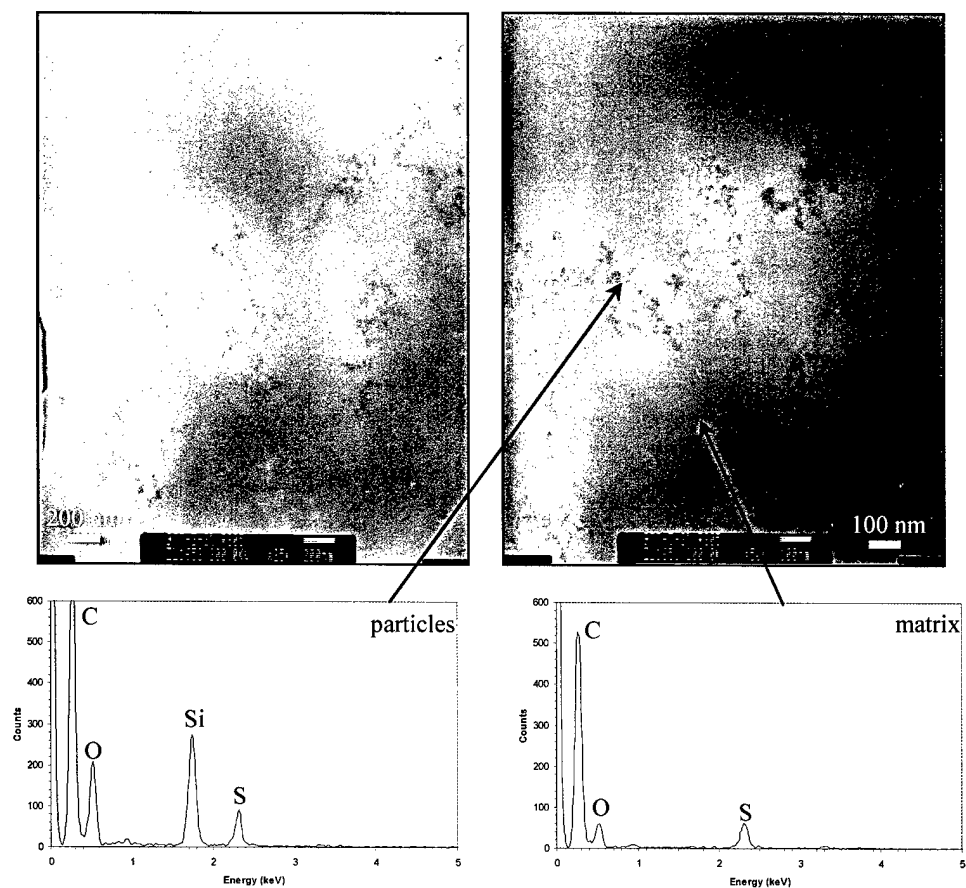
**Figure 11** TEM micrographs of 977-3/Aerosil® R202 (98/2) showing uniform dispersion of Aerosil® R202 aggregates in the 977-3 epoxy where scale bar is 100 nm (left) and 50nm (right). EDS analyses were also conducted on the TEM samples.



**Figure 12** TEM micrographs of 977-3/Aerosil® R202 (95/5) showing uniform dispersion of Aerosil® R202 aggregates in the 977-3 epoxy where scale bar is 500 nm (left), 200nm (center), and 100 nm (right)

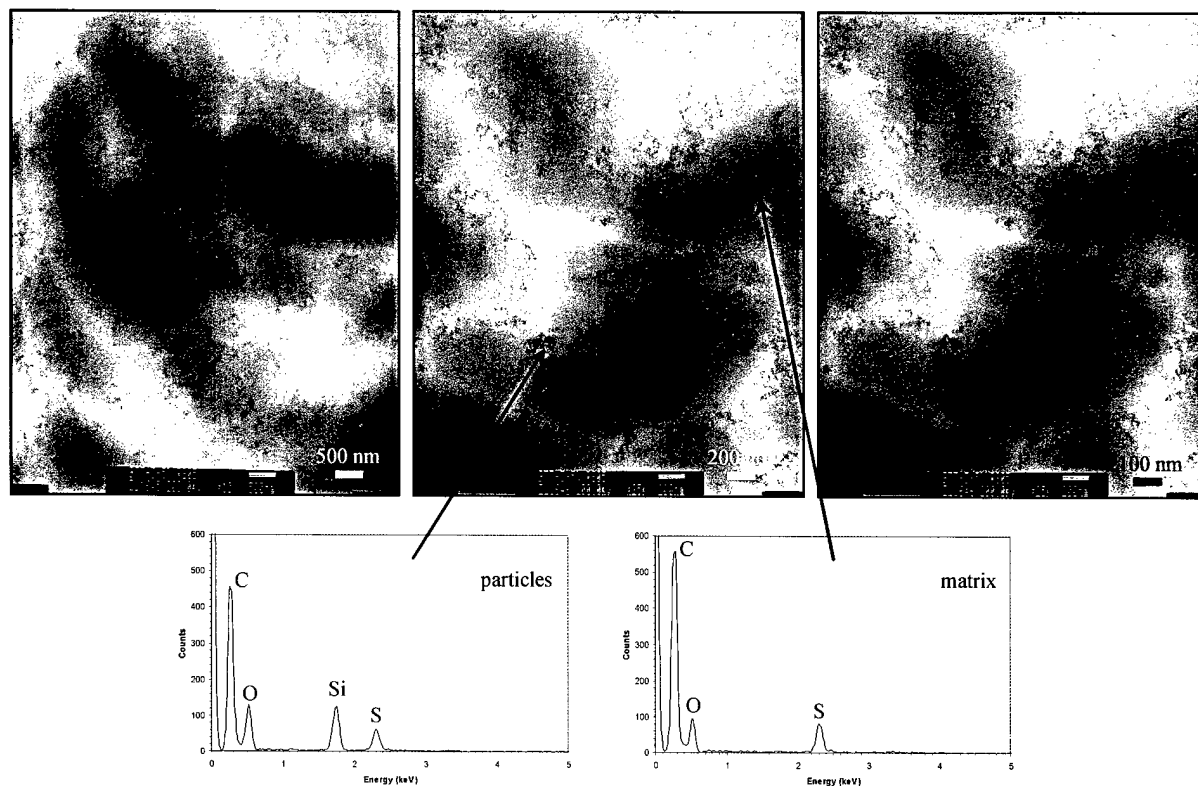


**Figure 13** DMTA analyses of 1%, 2%, and 5% Aerosil® R202 in 977-3



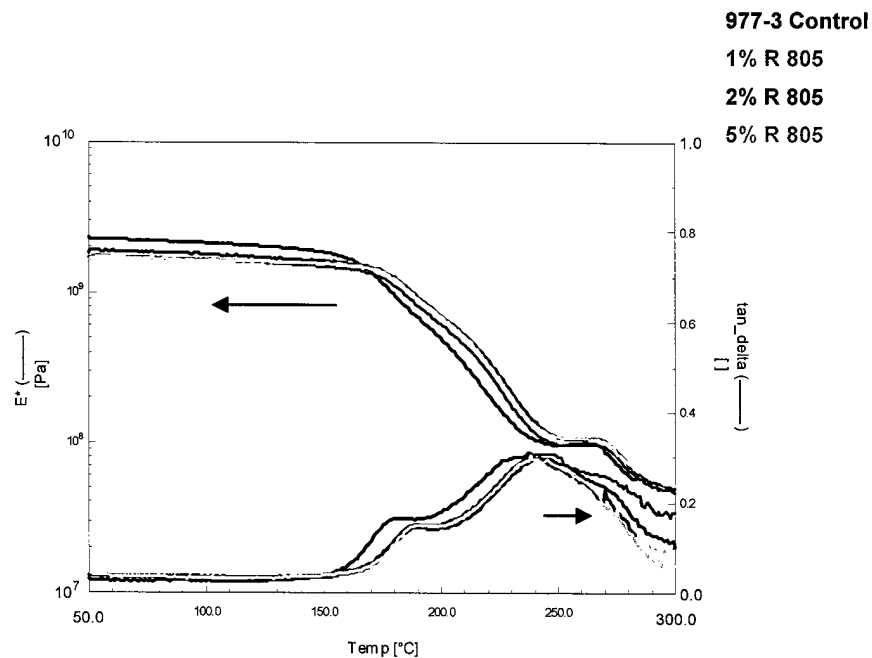
**Figure 14** TEM micrographs of 977-3/Aerosil® R805 (98/2) showing uniform dispersion of Aerosil® R805 aggregates in the 977-3 epoxy where scale bar is 200 nm (left) and 100 nm (right). EDS analyses were also conducted on the nanocomposite samples.





977-3+5% R805 Silica  
7/26/2004

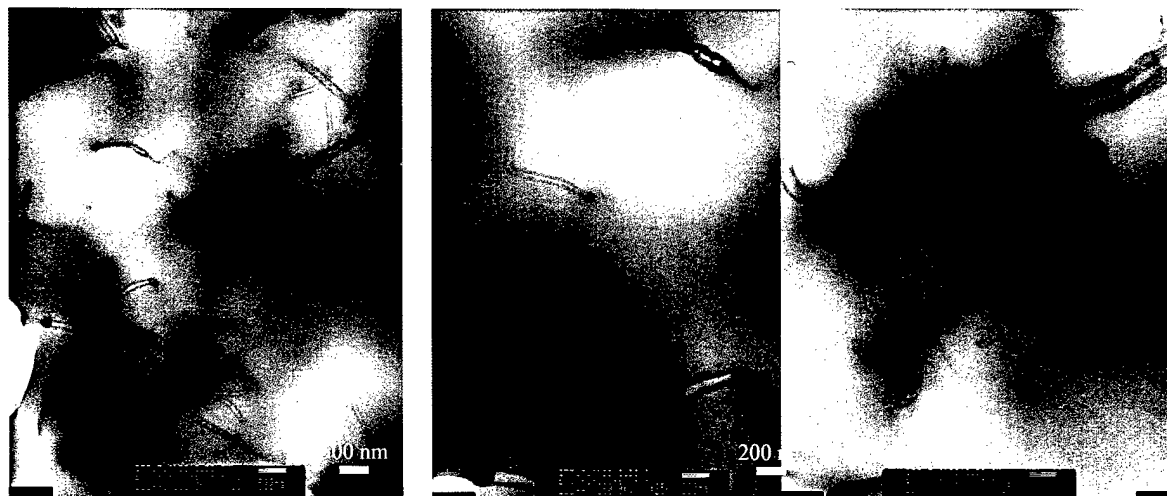
**Figure 15** TEM micrographs of 977-3/Aerosil® R805 (95/5) showing uniform dispersion of Aerosil® R805 aggregates in the 977-3 epoxy where scale bar is 500 nm (left), 200 nm(center), and 100 nm (right)



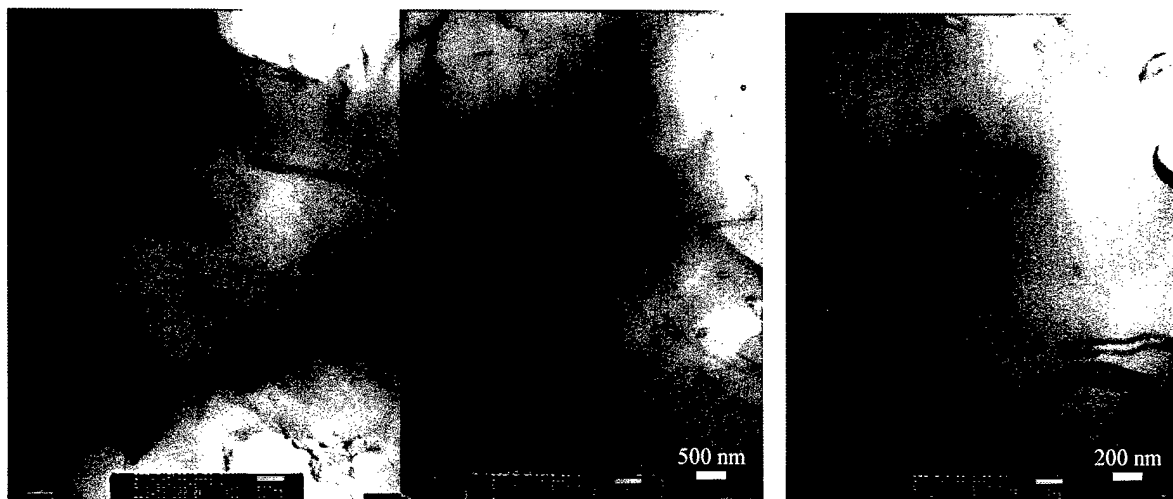
**Figure 16** DMTA analyses of 1%, 2%, and 5% Aerosil® R805 in 977-3 epoxy

**3.4 Processing and Characterization of 977-3/CNF Nanoparticle Systems** The 977-3 resin system was mixed with (99/1), (98/2), and (95/5) of PR-19-PS amine treated CNF; with (99/1), (98/2), and (95/5) of PR-19-PS CNF; and (99/1), (98/2), and (95/5) of PR-19-PS-Ox CNF. The PR-19-PS amine treated CNF sample reacted with the epoxy components of the 977-3 resin systems. Visual inspection showed large lumps of CNF was formed in the 977-3/PR-19-PS amine treated CNF mixtures. The PR-19-PS CNF mixtures also showed undesirable results. Figures 17 and 18 show the TEM micrographs of the 977-3/2% PR-19-PS-Ox CNF and 977-3/5% PR-19-PS-Ox CNF in progressive magnification. Figure 19 shows the DMTA analyses of the 977-3/1%, 2%, and 5% loadings of PR-19-PS-Ox CNF. The  $T_g$  was barely increased with increased loading of PR-19-PS-Ox CNF (5%), yet the complex modulus doubled (961 MPa) with the 5% PR-19-PS-Ox CNF.

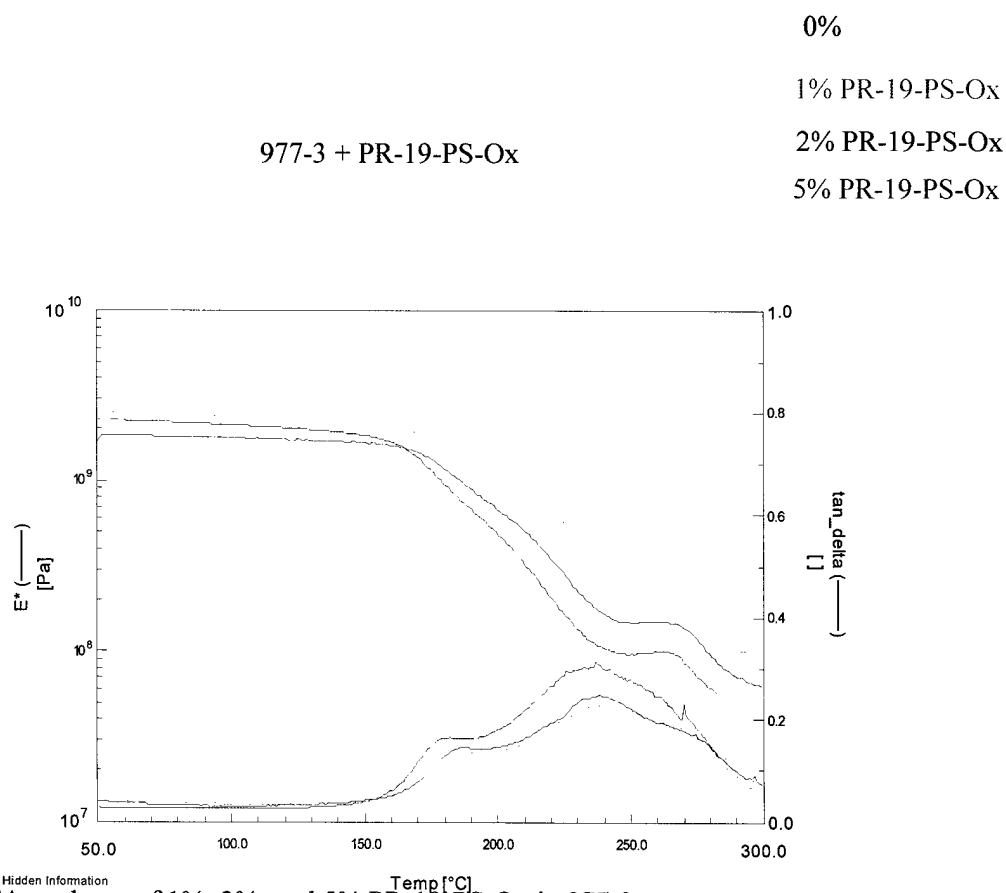
Table 11 summarizes the DMTA analyses for the neat epoxy nanocomposites as compared to the 977-3 control material. All the data is collected in three-point blending geometry with strain amplitude of 0.05%, frequency of 1 Hz and heating rate of 5°C/min. Using 1% of Cloisite® 10A nanoclay in the 977-3 resin system, a slight increase of 8° in  $T_g$  and a substantial increase of complex modulus were detected. The Cloisite® 30B nanoclay was not as effective as the Cloisite® 10A nanoclay in the 977-3 resin system. Using 2% Aerosil® R202 nanosilica in the 977-3 resin system, a substantial increase of 21° in  $T_g$  and a substantial increase of complex modulus were recorded. Using 1% of Aerosil® R805 nanosilica in the 977-3 resin system, a slight increase of 10° in  $T_g$  and a small increase of complex modulus were also detected. In general, all samples reinforced with nanosilica exhibit higher  $T_g$ . There was not much enhancement of  $T_g$  using PR-19-PS-Ox CNF in 977-3 resin system.



**Figure 17** TEM micrograph showing good dispersion of 2% PR-19-PS Ox CNF in the 977-3 resin



**Figure 18** TEM micrographs of 5% PR-19-PS CNF in 977-7 resin showing good dispersion of the CNFs in the resin.



**Figure 19** DMTA analyses of 1%, 2%, and 5% PR-19-PS-Ox in 977-3

**Table 11** Summary of DMTA analyses of Epoxy Nanocomposites

Material	Tg from E' C	Tg from E'' C	Tg from tan $\delta$ C	E* at 200C MPa
977-3 Control	172	176	237	483
1% Cloisite 10A	183	186	245	923
2% Cloisite 10A	186	185	245	786
5% Cloisite 10A	183	185	228	572
5% Cloisite 30B	164	166	221	390
1% Aerosil R202	178	178	242	609
2% Aerosil R202	188	187	258	964
5% Aerosil R202	186	184	245	702
1% Aerosil R805	183	184	247	620
2% Aerosil R805	182	186	243	711
5% Aerosil R805	185	186	238	697
1% PR-19-PS-Ox	178	186	236	670
2% PR-19-PS-Ox	180	188	238	688
5% PR-19-PS-Ox	180	190	241	961

**3.5 Scaling Up and Processing of NCPMC** Based on the TEM and DMTA analyses as well as literature data, six candidates were selected for scaling up of 20 lbs of 977-3/nanoparticle resin systems to produce prepreps at the CEM Winona, MN facility as follows:

- 977-3/Cloisite® 10A nanoclay in (98/2) wt%
- 977-3/Aerosil® R202 nanosilica in (98/2) wt%
- 977-3/Aerosil® R805 nanosilica in (98/2) wt%
- 977-3/PR-19-PS-Ox in CNF in (98/2) wt%
- 977-3/Aerosil® R202 nanosilica in (97/3) wt%
- 977-3 in (100) wt% with no nanofillers

**Processing Procedures** CEM uses the AS4-6K carbon fiber fabric recommended by Boeing Company [37]. It was used to produce prepreps for the above five NCPMCs and the baseline material. The carbon fabric is prepregged using solvent-based process at semi-production scale at the CEM Winona, MN facility using several pre-determined resin/nanofiller compositions. All panels are consolidated by vacuum bagging and autoclave cured at appropriate temperature cycles. Panels are physically characterized for dimensions and weight. At the completion of the processing, all panels are given a final characterization for density. A set of two 18- by 11- by 0.15-inch NCPMC panels were fabricated for each nanocomposite and 977-3/AS4-6K.

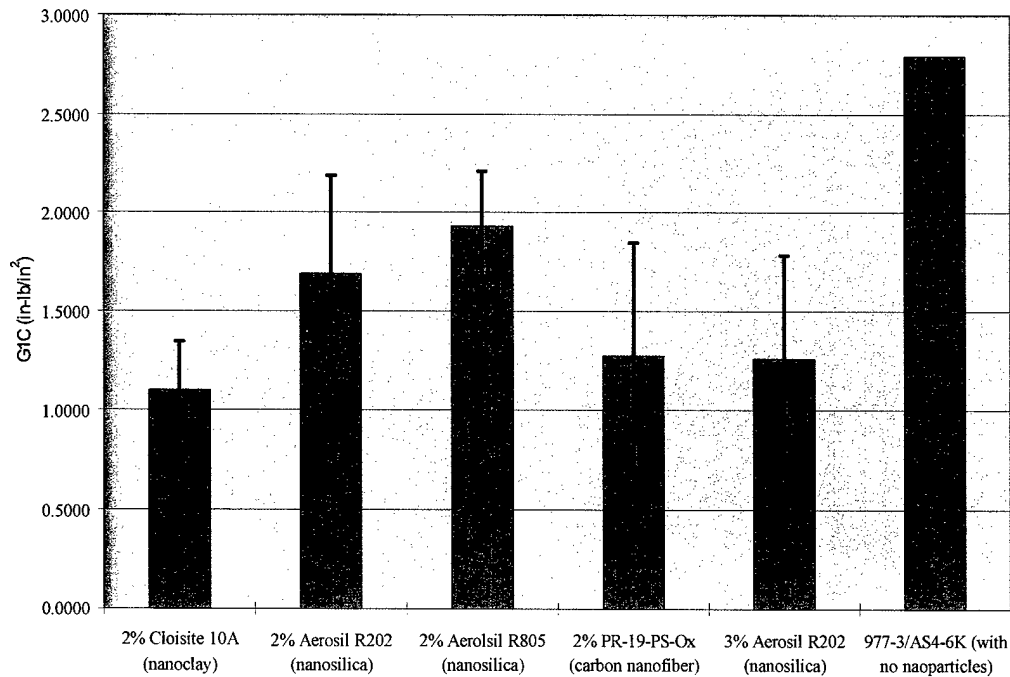
**3.6 Mechanical Properties of NCPMC** All six composite candidates were visually inspected and C-scanned to identify blisters (delamination defects) before machining. The following mechanical properties were obtained for each PMC material per ASTM specs:

- $G_{1C}$
- $G_{2C}$
- Flatwise tension strength (FWT)
- Short beam interlaminar shear strength (SBS)
- Flexural strength

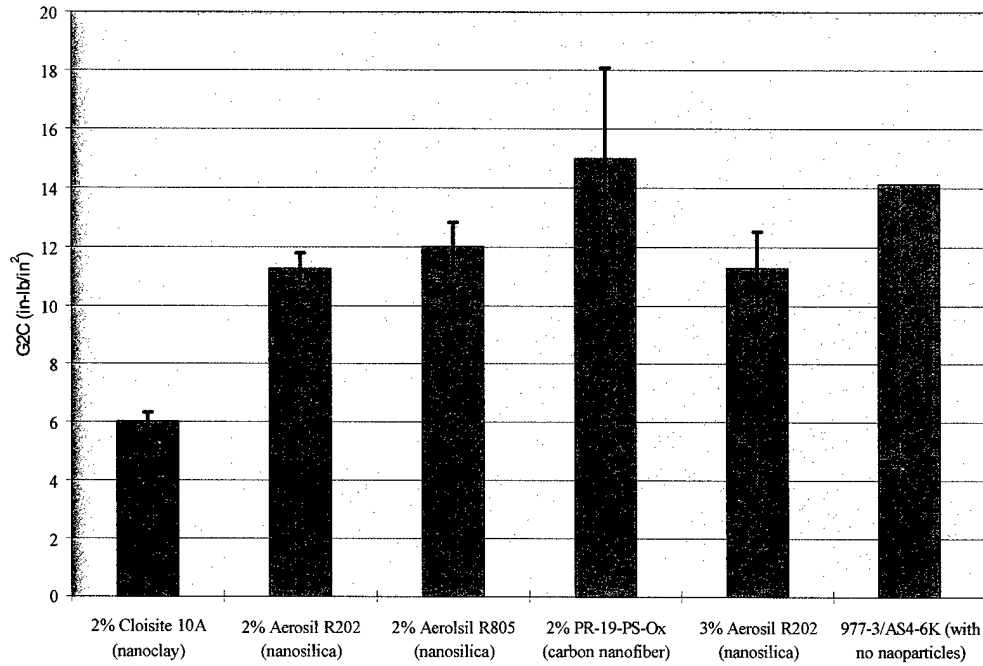
Table 12 summarizes the mechanical properties of the six materials. All mechanical property tests were conducted per ASTM using six specimens at the CEM Anaheim, CA and Winona, MN facilities.

**Table 12** Comparison of Mechanical Properties of the Six Materials

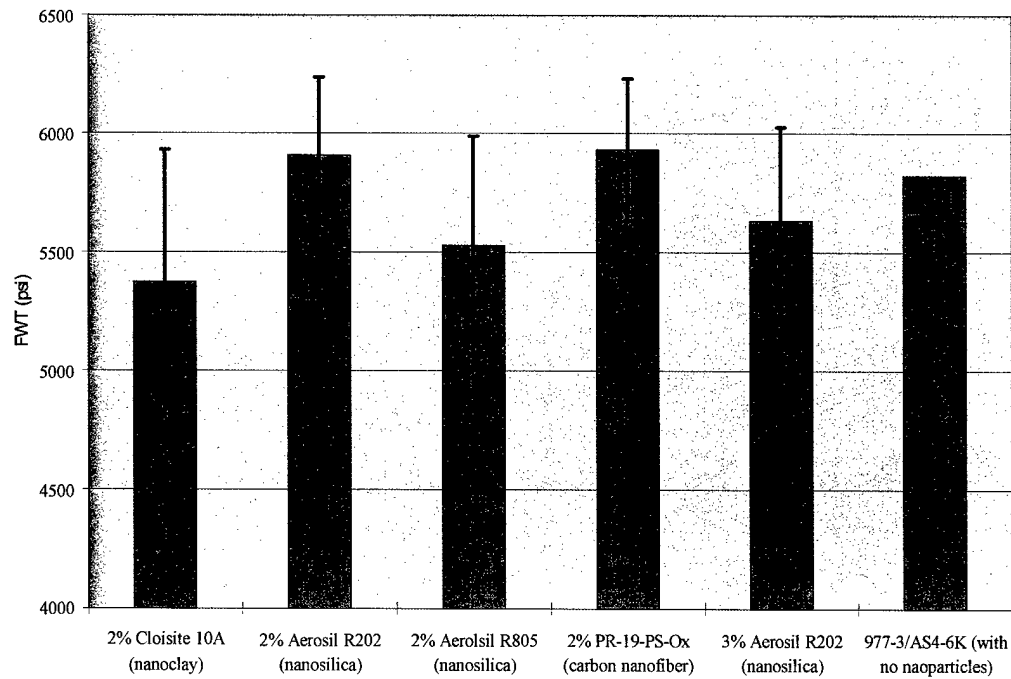
Material	$G_{1C}$ (in-lb/in <sup>2</sup> )	$G_{2C}$ (in-lb/in <sup>2</sup> )	FWT (psi)	Shear SBS (ksi)	Flexural Strength (ksi)
977-3/2% Cloisite® 10A PMC	1.10	6.02	5375	9.5	159
977-3/2% Aerosil® R202 PMC	1.69	11.26	5908	10.9	141
977-3/2% Aerosil® R805 PMC	1.93	12.02	5528	10.8	144
977-3/2% PR-19-PS-Ox CNF PMC	1.27	15.01	5932	12.7	142
977-3/3% Aerosil® R202 PMC	1.26	11.28	5631	13.7	155
977-3/AS4-6K baseline PMC	2.79	14.14	5823	11.7	150



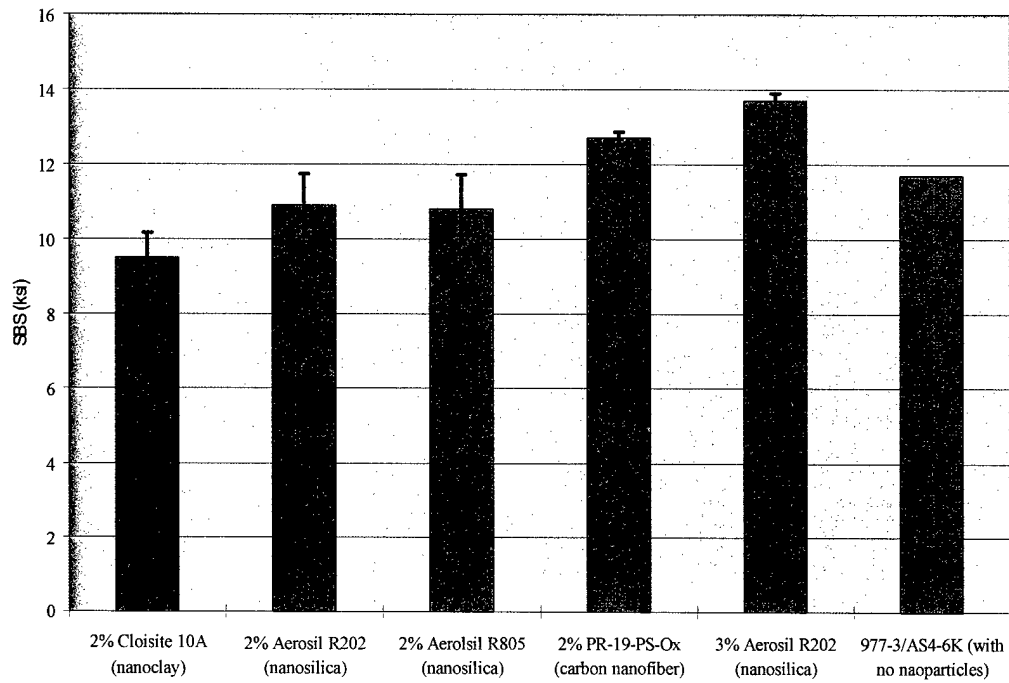
**Figure 20** Comparison of  $G_{1C}$  values of the five nanomodified epoxy carbon fiber-reinforced PMCs with the 977-3/AS4-6K baseline composite



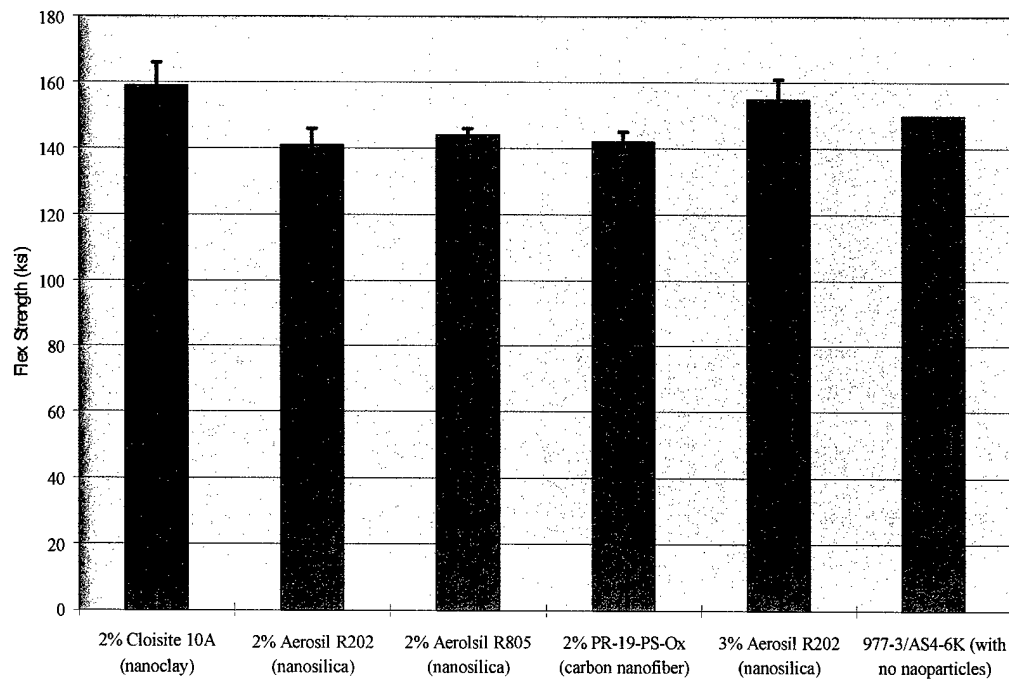
**Figure 21** Comparison of  $G_{2C}$  values of the five nanommodified epoxy carbon fiber-reinforced PMCs with the 977-3/AS4-6K baseline composite



**Figure 22** Comparison of FWT values of the five nanommodified epoxy carbon fiber-reinforced PMCs with the 977-3/AS4-6K baseline composite



**Figure 23** Comparison of SBS values of the five nanomodified epoxy carbon fiber-reinforced PMCs with the 977-3/AS4-6K baseline composite



**Figure 24** Comparison of flexural strength values of the five nanomodified epoxy carbon fiber-reinforced PMCs with the 977-3/AS4-6K baseline composite

#### 4. SUMMARY AND CONCLUSIONS

The CEM 977-3 toughened epoxy resin system was modified by three types of nanoparticles (MMT nanoclay, CNF, and nanosilica) at several different wt% loading levels (1%, 2%, and 5%) for this study. The TEM analysis was used to characterize the morphology of these resin systems and to screen candidates based on their degree of dispersion. DMTA analysis was also performed on selective neat epoxy nanocomposites. Based on the TEM and DMTA analyses as well as literature data, six candidates were selected to produce AS4-6K carbon prepreps in a semi-production scale at the CEM Winnoa, MN facility. Composites were fabricated and mechanical properties were determined at the CEM Anaheim, CA facility. A set of two 18- by 11- by 0.15-inch composite panels were fabricated for each candidate and for the baseline materials. Mechanical properties such as  $G_{1C}$ ,  $G_{2C}$ , flatwise tension strength (FWT), short beam interlaminar shear strength (SBS), and flexural strength were measured and compared with the 977-3/AS4-6K baseline material.

The following conclusions were drawn from this study:

1. DMTA data of the neat epoxy nanosilica nanocomposite (2% Aerosil® R202) show the highest  $T_g$  (258°C) and the highest complex modulus (964 MPa).
2. Impressive values ( $T_g$  and complex modulus) of neat nanocomposite resin with 2% Aerosil R202 did not carry over into the NCPMC.
3. The TEM analysis has been demonstrated as an effective tool to characterize and screen candidates based on their degree of dispersion.
4. DMTA analysis has also been demonstrated as an effective tool to characterize and screen candidates based on their mechanical properties.
5. MMT clay, nanosilica, and CNF dispersed very well in the epoxy components of the 977-3 resin system forming epoxy nanocomposites.
6. The  $G_{1C}$  values of all the epoxy nanocomposites were lower than the 977-3/AS4-K6 baseline material with the least knockdown with the 2% Aerosil® R805 nanosilica sample.
7. The  $G_{2C}$  values of all the epoxy nanocomposites were lower than the 977-3/AS4-K6 baseline material with the 2% PR-19-PS-Ox sample higher than the baseline material.
8. The FWT values of all epoxy nanocomposites were slightly lower than the baseline with 2% PR-19-PS-Ox and 2% Aerosil® R202 samples higher than the baseline material.
9. The SBS values of all epoxy nanocomposites were slightly lower than the baseline with 3% Aerosil® R202 and 2% PR-19-PS-Ox CNF higher than the baseline.
10. The flexural strength of all epoxy nanocomposites were slightly lower than the baseline with the 2% Cloisite® 10A and 3% Aerosil® R202 samples higher than the baseline.
11. Mechanical testing of NCPMC by CEM involved measuring different composite characteristics than the neat resin.
12. Cloisite 10A was an inferior nanofiller for 977-3.
13. Microstructure analyses of pre- and post-test NCPMC specimens would allow more fundamental understanding of nanostructured material behavior.
14. It is suggested to possibly combine Aerosil R202 with PR-19-PS-Ox CNF.

#### 5. REFERENCES

1. R.A. Vaia, *Amptiac Quarterly*, 6 (1), 17 (2002).
2. E.P. Giannelis, *Adv. Materials*, 8, 29 (1996).



3. J.H. Koo *et al.*, *Proc. SAMPE 2002*, SAMPE, Covina, CA, 2002, p. 1085
4. J.H. Koo *et al.*, SAMPE 2003, Long Beach, CA, May 12-15, 2003.
5. J.H. Koo *et al.*, unpublished data of TPU nanocomposites, Apr. 2003.
6. J.D. Lichtenham *et al.*, *Macromolecules*, **26**, 2141 (1993).
7. M.L. Lake *et al.*, *Proc. SAMPE 2002*, SAMPE, Covina, CA, 2002, p. 1794
8. M.R. Nyden, J.W. Gilman *et al.*, *Proc. SAMPE 2002*, SAMPE, Covina, CA, 2002, p. 738.
9. C.T. Vogelson, Y. Koide, L.B. Alemany, and A.R. Barron, *Chem. Mater.*, **12** 795 (2000); U.S. Patent 6,369,183 dated April 9, 2002.
10. C. Zilg *et al.*, U.S. Patent 6,197,849 dated April 6, 2001.
11. Tie Lan *et al.*, U.S. Patent 6,251,980 dated June 26, 2001.
12. E.N. Gilbert, B.S. Hayes, and J.C. Seferis, *Proc. SAMPE 2002*, SAMPE, Covina, CA, 2002 p. 41.
13. S. Spindler-Ranta and C.E. Bakis, *Proc. SAMPE 2002*, SAMPE, Covina, CA, p. 1775.
14. C. Chen and D. Curliss, *SAMPE J.*, **37** (5), 11 (2001).
15. B.P. Rice, C. Chen, L. Cloos, and D. Curliss, *SAMPE J.*, **37** (5), 7 (2001).
16. C. Chen and D. Curliss, *Mat. Res. Soc. Symp. Proc.* Vol. 703, MRS, Warrendale, PA, 2002, p. V1.2.
17. O. Becker, R. Barley, and G. Simon, *Polymer*, **43** 4365 (2002).
18. O. Becker, Y-B. Cheng, R.J. Varley, and G.P. Simon, *Macromolecules*, **36** (5), 1616 (2003).
19. A. Lee, *Proc. POSS Nanotechnology Conference*, Huntington Beach, CA, Sept 25-27, 2002.
20. C. Pittman, *Proc. POSS Nanotechnology Conference*, Huntington Beach, CA, Sept 25-27, 2002.
21. J.M. Brown, D. Curliss, and R.A. Vaia, *Chem. Mater.*, **12** 3376 (2000).
22. C.S. Triantafillidis, P.C. LeBaron, and T.J. Pinnavaia, *J. Solid State Chemistry*, **167**, 354 (2002).
23. C.S. Triantafillidis, P.C. LeBaron, and T.J. Pinnavaia, *Chem. Mater.*, **14**, 4088 (2002).
24. C. Pederson, Cytec Engineered Materials, Anaheim, CA, personal communication, 3/03 and CYCOM® 977-3 resin system technical data sheet.
25. R. Krishnamoorti and R.A. Vaia, Ed., *Polymer Nanocomposites: Synthesis, Characterization, and Modeling*, ACS Symposium Series 804, ACS, Washington, DC, 2001.
26. B. Powell, Southern Clay Products, Gonzales, TX, personal communication 4/2003 and Cloisite® 30B technical data sheet.
27. Cloisite® 10A technical data sheet, Gonzales, TX.
28. G.G. Tibbetts, *J. Crystal Growth* 1984; 66:632.
29. M.L. Lake, J-M. Ting. In *Carbon Materials for Advanced Technologies*, T.D. Burchell, Ed., Pergamon, Oxford: England, 1999.
30. M.L. Lake, manuscript from Applied Sciences, Inc., Cedarville, OH, 11/2002.
31. B. Maruyama and K. Alam, *SAMPE J.*, **38** (3), 59 (2002).
32. Applied Sciences, Inc. amino modified CNF.
33. Technical Bulletin No. 27 AEROSIL for Solvent-Free Epoxy Resin, AEORSIL Technical Service Dept., Degussa AG, D-63403 Hanau-Wolfgang, Germany.

34. AEROSIL® R805 technical data sheet, Degussa AG, D-63403 Hanau-Wolfgang, Germany.
35. AEROSIL® R202 technical data sheet Degussa AG, D-63403 Hanau-Wolfgang, Germany.
36. F. Yang, R.A. Yngard, G.L. Nelson, "Nanocomposites 2002," San Diego, CA, Sept 23-5, 2002.
37. F.C. Campbell, personal communication, Boeing Company, St. Louis, MO, 4/2004.

## **ACKNOWLEDEMENTS**

This work was sponsored by Air Force Office of Scientific Research (AFOSR) under AFOSR Contract No. F49620-03-C-0093 (STTR Phase I) with Dr. Charles Y-C Lee as our Program Manager. The authors would like to thank M. Lake of Applied Sciences, Dr. D. Hunter of Southern Clay Products, and Dr. Z.P. Luo of Texas A&M University for supporting the program.